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(54) **Polyvinyl Alcohol Synthetic
Fibres**

(57) The adhesion of synthetic fibres of polyvinyl alcohol (PVA), particularly to cement, is improved by incorporating a granular calcium compound into an aqueous solution of PVA to form a mixed spinning

solution, spinning the latter and, after drawing and heat treating the resulting fibres, immersing them in an acid or alkali to elute a part of the calcium compound and thereby produce a fibre with a surface having elongated crack-like cavities.

Such fibres are readily incorporated into cements to strengthen objects made of the cement.

GB 2 073 653 A

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Figure 1

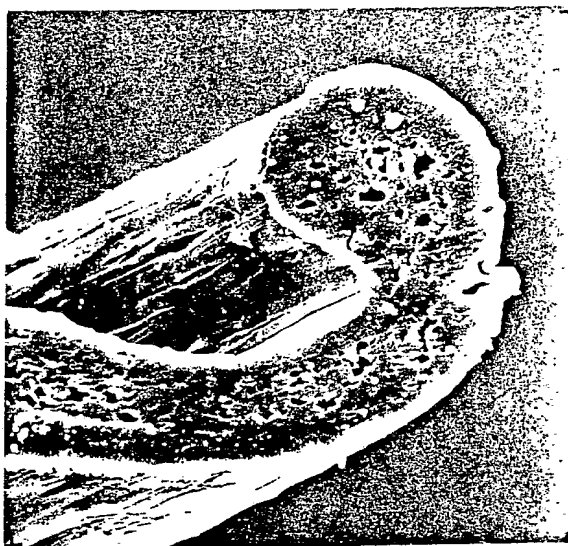


Figure 2



Figure 3

SPECIFICATION

Polyvinyl Alcohol Synthetic Fibers and Their Production

This invention relates to polyvinyl alcohol synthetic fibres (PVA fibres) and their production. More particularly and indeed exclusively, the PVA fibres are used in reinforcing cement articles.

5 Cement, gypsum, and other materials that are hardened by hydration have hitherto been used for preparing such articles as roof, wall or floor coverings, concrete blocks, cement tiles, pavement and concrete pipes. As is well known, such cement articles are usually reinforced with fibres in order to improve, *inter alia*, their bending, tensile and impact strength. While asbestos fibres have most typically been used for reinforcing cement articles, it has also been common recently to use inorganic materials, 10 such as steel or glass fibres, and organic synthetic fibres such as polypropylene, polyamide and polyvinyl alcohol, either individually or in combination.

A cement article having a small thickness has a considerably improved strength if it is reinforced by 15 to 35% of asbestos fibres, but its impact strength is still unsatisfactory. The use of asbestos involves other disadvantages. It is unlikely to exert an adverse effect on the human body from a health 15 standpoint. As it is a substance occurring in nature, it becomes more and more costly. This is naturally likely to result in an increased cost of manufacture of cement articles reinforced with asbestos fibres.

Among glass fibres, E-glass is useless for reinforcing cement, since cement is strongly alkaline and corrodes E-glass fibres. Alkali-resistance glass fibres have recently been developed, but they are expensive, and though they are certainly resistant to alkalis, their durability is not satisfactory. 20 Moreover, they are very brittle, and easily broken when dispersed in water or mixed with cement. Accordingly, they are not satisfactory for reinforcing cement.

It is known that natural or synthetic fibres, such as pulp, cellulose, cotton, polyamide, polyester, and polyolefin, can be incorporated into a cement aggregate, either instead of asbestos fibres or together with asbestos fibres in order to reduce the quantity of asbestos fibres required. These fibres do 25 not, however, help to improve the folding endurance of cement products, though they can effectively improve the impact strength of a cement product or the handling properties of a green sheet of cement and prevent formation of any hair crack in it.

The reinforcement of a cement product by a fibrous material involves a relatively complicated mechanism, but if it is discussed in a simplified version, there appear to be two aspects which have to 30 be considered. One of them is concerned with the amount of external stress to be borne by the reinforcing material. If any stress from an external source, such as tensile force, is applied to a composite formed by cement as a matrix and reinforcing material, it is borne partly by the matrix and partly by the reinforcing material. If a sufficient degree of adhesion is maintained between the matrix and the reinforcing material, the various properties of the composite can be considered as the sum of 35 the properties of the matrix and the reinforcing material. The stress borne by the reinforcing material may be expressed as $V_f \epsilon_c E_f$, in which V_f stands for the volume fraction of the reinforcing material, E_f stands for its Young's modulus, and ϵ_c stands for the distortion (strain) of the composite. Accordingly, if the value of V_f is constant, and if the properties of the cement aggregate are constant, an increase in the value of E_f brings about an increase in the amount of stress to be borne by the reinforcing material, 40 hence an improved strength of the composite.

The other aspect to be taken into consideration is the reinforcing efficiency of the reinforcing material. While there are a number of secondary factors such as the degree of dispersion or orientation of the reinforcing material in the matrix, a most fundamental problem resides in the strength of an 45 interfacial bond which is obtained between the matrix and the reinforcing material by adhesion or frictional force.

The maximum tensile strength (i.e., breaking strength) of the reinforcing fibre-cement composite may be expressed by the following equation:

$$\sigma_c = \sigma_m (1 - V_f) + \sigma_f V_f$$

50 in which σ_m and σ_f stand for the amounts of stress bearing on the matrix and the fibres, respectively. The following relationship is established between the adhesion strength τ of the fibres to the cement matrix and their tensile stress σ_f :

$$\sigma_f = \frac{\tau l}{d}$$

in which D and l stand for the diameter and length, respectively, of the fibres. In view of the orientation factor of the fibres, the following equation is derived:

$$\sigma_c = A \sigma_m (1 - V_f) + B \tau \frac{l}{d} V_f$$

in which A is a constant which can theoretically have a maximum value of 1, and B is a constant having a value which depends on the degree of orientation of the fibres in the direction of their tensile stress.

According to this equation, it is possible to increase the value of σ_c if the value of B is increased, but the latter value depends on the method by which the composite is used or worked. Therefore, it is more

5 effective to increase the value of τ in order to improve the efficiency of the fibres for reinforcing 5 cement.

In view of the mechanism of reinforcement as hereinabove discussed, it is necessary that the reinforcing material having a high Young's modulus and a high strength, and that the reinforcing material and the cement matrix have a highly strong interfacial bond between them. In other words, if

10 no satisfactory adhesion is maintained between the reinforcing material and the matrix, no satisfactory 10 reinforcement can be expected, however high the Young's modulus and strength of the reinforcing material may be.

Referring now to cement reinforced with PVA fibres, a method of manufacturing a sheet of fibre-reinforced cement by a wet sheet-making process using a combination of high-strength PVA fibres and

15 asbestos fibres, or PVA and glass fibres. The use of such PVA fibres having a high Young's modulus 15 appears to be effective for providing a cement product of high quality by eliminating the various fundamental drawbacks of other organic or inorganic reinforcing fibres. However, our investigations indicate that the known method does not provide a sufficiently strong bond between the fibres and the cement, and the reinforcing fibres therefore do not appear to exhibit their function to the full extent.

The present invention is based on the discovery of certain PVA fibres that are essentially useful

20 for the production of a satisfactorily reinforced cement product and that replace the PVA fibres of high 20 strength and Young's modulus required in the prior art. The fibres used in accordance with the invention have a very high strength of adhesion to the cement. They are also inexpensive and can be manufactured at a lower cost than any known PVA fibres of high strength and Young's modulus.

As already pointed out, the interfacial adhesion between the matrix and the reinforcing fibres is a

25 very important factor in determining the performance of a fibre-reinforced cement product. A variety of 25 methods are known for obtaining such interfacial adhesion either chemically or physically. Among chemical methods, for example, the use for reinforcing purposes of synthetic fibres having surfaces to which a substance reactive with cement, such as colloidal silica or alumina, has been applied, is

known. These fibres, however, fail to achieve any satisfactory adhesion to cement, which does not

30 satisfactorily adhere to the fibre surfaces, or is very easily peeled off the fibres. The use is also known of 30 melt-spun fibres into which cement has been kneaded in order to obtain an improved chemical bond between the fibres and the cement. This method, however, fails to provide any practically acceptable result for the reinforcement of cement with fibres. All of these known methods use polyamide or

polyolefin fibres, which can be obtained by melt spinning, but as these synthetic fibres are

35 hydrophobic *per se*, they can not be expected to achieve any satisfactory adhesion or chemical bond to 35 cement. Among known physical methods, a pulsating flow of the spinning solution can be caused during the spinning operation, or ultrasonic waves or other external force can be applied to the fibres during their solidification, to create unequal fineness of the fibres, or the fibres can be formed with

spherical ends or an irregular cross section in order to impart the so-called anchor effect to the fibres.

40 All of these methods are, however, unrealistic, since they deform the fibres to an extent that is more 40 than acceptable. Moreover, it is basically impossible to expect any satisfactory adhesion of the fibres, which are composed of an organic high-molecular-weight elastic substance liable to heavy plastic deformation, to the cement matrix, even if any attempt is made by deforming the fibres to prevent their

slipping from the matrix, insofar as those fibres are originally not adhesive to cement.

45 45

In accordance with the invention, basically hydrophilic PVA fibres for reinforcing cement are spun from a mixture of an aqueous polyvinyl alcohol solution and a calcium compound having a high affinity for cement and forming the nuclei of cement crystals during the hydration of cement, and a multiplicity of crack-like concavities are formed in the fibre surfaces so that voids extending into the interior of the

50 fibres may be formed and calcium may be present in the surfaces and interior of those concavities. 50 Those voids contribute to anchoring cement in the fibres during its hydration, and the presence of a calcium compound serves to create a strong bond between the fibres and the matrix.

According to one aspect of this invention, there are provided polyvinyl alcohol synthetic fibres having an improved property of adherence to cement and obtained by the mixed spinning of polyvinyl

55 alcohol and a granular calcium compound that is insoluble or sparingly soluble in water, the fibres 55 having, formed on their surfaces, a multiplicity of crack-like concavities formed by elution (dissolution) of the calcium compound after formation of the fibres, the fibres also having a void volume of 0.1 to 0.5 cm³/g and containing at least 0.2% by weight of calcium based on polyvinyl alcohol.

According to another aspect of this invention, there is provided a method of manufacturing

60 polyvinyl alcohol synthetic fibres having an improved property of adherence to cement, that comprises 60 incorporating a granular calcium compound having a particle size of 0.05 to 10 microns and insoluble or sparingly soluble in water into an aqueous solution of polyvinyl alcohol to prepare a mixed spinning solution containing 5 to 50% by weight of the calcium compound based on polyvinyl alcohol, spinning the mixture to form fibres, drawing and heat treating the fibres and immersing them in an acid or alkali

to elute the calcium compound so that the resulting fibres contain at least 0.2% by weight of the calcium based on polyvinyl alcohol.

When proceeding according to this invention, the calcium compound is removed from the fibres in an appropriate manner to provide them with an increased void volume, while at the same time ensuring that the fibres contain an appropriate quantity of calcium. If too much calcium compound is removed, the fibres have a rougher surface, which might be expected to anchor the cement more effectively, but which also means a reduction in the strength of a bond between the fibres and the cement. The removal of more than 95% of calcium is not desirable, since the remaining calcium can no longer be expected to maintain any satisfactory adhesion of the fibres to the cement. Neither is the removal of calcium in any proportion below 5% desirable, since there are too few crack-like concavities and it is impossible to form a sufficiently rough fibre surface to expect any satisfactory anchoring effect of the fibres for the cement, even though the fibres may have a high affinity for the cement. Thus, the degree to which calcium is removed from the fibres has opposite effects on the adhesion of the fibres and on the anchor effect of the roughened fibre surfaces.

Any void volume less than 0.1 cm³/g fails to distinguish the fibres from any ordinary fibre, and would not be expected to provide any anchor effect as a result of roughened fibre surfaces, while any void volume of the fibres exceeding 0.5 cm³/g leads to a drastic reduction in the strength and Young's modulus of the fibres. It has been found that the fibres are required to contain at least 0.2% by weight of calcium based on polyvinyl alcohol, and have a void volume of 0.1 to 0.5 cm³/g in order to maintain their effective adhesion to cement and to provide the fibre surfaces with crack-like concavities to a sufficient degree to enable them to exhibit a satisfactory anchor effect.

Referring to the adhesion between the fibres and the cement, the setting and hardening mechanisms of a cement gel are not clear, but the adhesion between the fibres and the cement is considered to be attributable to the adherence to the fibres of hydration products formed as a result of the very active hydration of gypsum, 3CaO · SiO₂ and 3CaO · Al₂O₃ eluted from a cement paste, the formation of calcium hydroxide and crystals containing Al⁺⁺⁺, Fe⁺⁺⁺ and SO₄⁻ ions, and their hydration with the calcium compound in the fibres.

The fibres of this invention are by way of example shown in Figures 1, 2 and 3 which are all electron microphotographs showing squares of actual size 33.3 μm. Figures 1 and 2 show that the fibres are formed on their surfaces with a multiplicity of crack-like concavities extending along their axes, and that they are also provided internally with a lot of hollow spaces. Figure 3 is an electron microphotograph showing the fibre surface exposed on a broken surface of a cement reinforced with fibres of this invention. The photograph indicates the growth of cement crystals around the fibres.

The fibres of this invention permit of growth of cement crystals on their surfaces to an extent that can be observed through an electron microscope, and exhibit a much higher reinforcing effect than that of any prior proposals.

The PVA fibres of this invention, which are roughened on their exterior and even interior surfaces, can be manufactured by a wet or dry spinning process, or even from a film of PVA, as any known PVA fibre can. It is, however, more usual to spin wet or dry. The spinning solution may contain 8 to 25% by weight of a mixture of PVA and a granular calcium compound for the wet spinning operation, and 25 to 60% by weight of such a mixture for the dry spinning operation. The aqueous PVA solution from which the spinning solution is prepared may contain 4 to 25% by weight of PVA for preparing the spinning solution of the wet spinning operation, and 15 to 60% by weight of PVA for the dry spinning operation. Any deviation from these ranges fails to provide an appropriate range of viscosity to the spinning solution, resulting in a reduction of fibre drawability, and hence a sharp reduction of the operating efficiency.

The granular calcium compound to be incorporated into the aqueous PVA solution may have a particle size of 0.05 to 10 microns, be insoluble or sparingly soluble in water, and be uniformly suspendable in the PVA solution. More specifically, it may be selected from among those mentioned below by way of example. It is possible to use a carbonate, such as natural calcium carbonate obtained by crushing limestone, calcite or oyster shells mechanically, or synthetic calcium carbonate produced chemically from limestone or sodium carbonate. It is also possible to use a sulphate, such as calcined gypsum, synthetic calcium sulphate, or gypsum produced from a desulphurising process. It is also possible to use calcium hydroxide (slaked lime). It is also possible to use any other natural or chemically synthesised calcium compound that is insoluble or sparingly soluble in water.

If the calcium compound has a particle size exceeding 10 microns, its particles are likely to block a filter or nozzle during the spinning operation, and thus cause the fibres to break easily when drawn. If its particle size is less than 0.05 micron, there is virtually no problem involved in the spinning or drawing of fibres, but if they are so small as to be highly uniformly distributed separately from one another without undergoing any coagulation, the surfaces of the resulting PVA fibres will have only a very small degree of unevenness or roughness, which will not greatly contribute to improving the reinforcing effect of the PVA fibres. It is therefore necessary to use a granular calcium compound having a particle size of 0.05 to 10 microns, preferably 0.2 to 5 microns.

The calcium compound is uniformly suspended in an aqueous PVA solution in a quantity of 0.5 to 50%, preferably 10 to 40%, by weight of PVA. If the amount of the calcium compound is below 0.5%

by weight of PVA, it may fail to provide the fibres with any satisfactory adhesion to cement, while any amount exceeding 50% by weight should also be avoided, since it is likely to bring about obstruction to the filtration of the spinning solution, blocking of the nozzle, reduction in spinnability, or fibre breakage during the drawing operation.

- 5 The spinning solution is prepared under the foregoing conditions, and may be formed into fibres 5
by a wet or dry spinning process, as is the case with any ordinary known PVA fibres. The wet spinning
process may be carried out by (1) introducing an aqueous PVA solution into an aqueous coagulating
bath containing a highly concentrated coagulating salt, (2) introducing the aqueous PVA solution into a
10 coagulating bath containing a highly concentrated aqueous solution of an alkali, or (3) adding boric 10
acid to the PVA solution, and introducing it into a coagulating bath containing an aqueous solution of a
salt that is alkaline. Any of these methods can be used, provided that the spinning solution and the
granular calcium compound are selected so as not to cause any trouble in the spinning operation.

- The method mentioned at (1) above is the commonest process for the wet spinning of PVA. It is
inexpensive to carry it out, and it provides a great advantage in the manufacture of PVA fibres for
15 reinforcing cement, as calcium carbonate and calcium silicate are also very inexpensive. According to 15
this spinning process, the spinning solution is spun into a bath of sodium sulphate and solidified, and
the resulting fibres are wet drawn, dried drawn again, and heat treated, followed by acetalisation if
required.

- Whether the wet or dry spinning process is used, it is necessary for the PVA fibres to be drawn up
20 to a total draw ratio in the range 6:1 to 16:1 in order to obtain the essential properties of the fibres, i.e., 20
strength and Young's modulus as required, resistance to hot water and to shrinkage in water, and
cracks formed as a result of the calcium particles. If their total draw ratio is less than 6:1, their strength
and Young's modulus and their resistance to hot water and to shrinkage in water are also reduced. Any
total draw ratio exceeding 16:1 should also be avoided, since it is likely to cause troubles such as
25 napping or breakage of the fibres or their entanglement on the rollers, thus reducing the operating 25
efficiency. A preferable total draw ratio of the fibres is in the range of 7:1 to 15:1.

- The fibres are then immersed in an acid or alkali for appropriate removal of calcium by elution or
dissolution to form cracks in the fibre surfaces. If the fibres are treated with an acid, it is possible to use
a mineral acid such as sulphuric acid, hydrochloric acid or nitric acid, and if they are treated with an
30 alkali, it is possible to use, for example, sodium hydroxide or potassium hydroxide. As PVA is easily 30
swollen and dissolved in a mineral acid, it is necessary to add to the treating bath a water-soluble
material, e.g. a salt or alcohol, that can effectively coagulate PVA. It is usually possible to use a
sulphate such as sodium sulphate, ammonium sulphate or magnesium sulphate, or a water-miscible
organic solvent such as methanol or acetone, as an agent for coagulating the PVA.

- 35 The acid treating bath should contain 5 to 400 g of acid per liter, and the alkali treating bath 30 35
to 300 g of alkali per liter. The acid treating bath should also contain 0.5 to 3 mols of a PVA
coagulating agent, e.g. sodium sulphate, per liter. The acid or alkali treating of the fibres may be carried
out at a temperature in the range room temperature to 90°C for a period of one minute to one hour,
depending on the reaction temperature and the fineness of the fibres. The following table shows by
40 way of example the calcium compound to be mixed with the fibres, and the agents for treating the 40
fibres for calcium removal.

	<i>Calcium compound</i>	<i>Treating agent</i>	
45	Natural calcium carbonate	Sulphuric acid and sodium sulphate	45
	Synthetic calcium carbonate	Sulphuric acid and sodium sulphate	
	Calcium sulphate	Sulphuric acid and sodium sulphate, or sodium hydroxide and sodium sulphate	
	Calcium silicate	Sulphuric acid and sodium sulphate	
	Slaked lime	Sulphuric acid and sodium sulphate	

- 50 Although each combination shown in the table uses only a single calcium compound, it is of 50
course possible to use a mixture of two or more calcium compounds.

- When the foregoing treatment is performed, it is necessary to ensure that the fibres contain at
least 0.2% by weight of calcium based on PVA, and have a void volume of 0.1 to 0.5 cm³/g.
Accordingly, it is necessary to choose the conditions for the treatment so that they ensure preservation
55 of 5 to 95% (i.e. removal by dissolution of 95 to 5%) of the calcium compound initially added. 55

- After the treatment for calcium removal has been finished, the fibres are neutralised, washed with
water, and dried, after which they may be treated with a finishing oil agent if required. If further
required, it is possible to subject the fibres to hydrophobic and crosslinking treatment after calcium
removal in order to improve their wet performance. This crosslinking treatment is well known as
60 acetalisation, and a bath for acetalisation can be used for conducting the aforesaid acid treatment and 60
the acetalisation of the fibres simultaneously. It is possible to use for acetalisation purposes
monoaldehydes, dialdehydes or polyaldehydes, which are usually used for acetalisation of PVA fibres,

or other crosslinking agents such as N-methylol compounds, epoxy compounds and diisocyanate compounds, or inorganic chelating agents.

The fibres of this invention can also be manufactured in accordance with a dry spinning process known for PVA fibres. They are spun, dried, heat treated, treated with an acid or alkali for removal of calcium by dissolution, and washed with water, followed by treatment with an oil agent if required.

Fibres manufactured as hereinabove described were buried in cement for withdrawal tests. They prove to be far more resistance to withdrawal from the cement than expected. A cement product in which the fibres of this invention are dispersed shows a greatly improved bending strength. Although quite a lot of questions still remain to be clarified in connection with the hardening mechanism of cement and the mechanism by which an interfacial bond is formed between the cement matrix and the reinforcing fibres, the unexpected results of this invention are apparently attributable to the appropriate removal from the fibres of the substance added to the spinning solution, or reaction products, thereby creating roughened fibre surfaces through which the cement penetrates into the fibres, and is bonded to them by virtue of a sort of anchor effect, and the contribution of the calcium compound in the fibres to improving the adhesion between the fibres and the cement. The results of this invention are surprisingly greater than what can be obtained by any known chemical or physical method intended for improving the adhesion between the fibres and the cement.

The PVA fibres of this invention can be incorporated into the cement matrix alone, or in combination with inorganic fibres such as asbestos, glass, mica or metal fibres in order to render the cement heat-resistance and fireproof. If a fibrillated fibrous material, such as pulp, is mixed or combined with the fibres of this invention, they can more effectively be distributed in cement to provide a product of improved performance. The fibres of this invention are applicable to the whole of a cement product or structure of which a certain level of bending strength is required, or locally to any portion of it. If they are used in combination with steel reinforcing members or frames, they are, of course, effective for preventing any local cracking of a concrete product. Moreover, the fibres have an appropriate degree of elongation to drastically improve the impact resistance of a cement product.

As is apparent from the foregoing description, this invention enables one to obtain an improved adhesion between cement and reinforcing fibres by virtue of (a) a multiplicity of crack-like concavities and voids formed in the surfaces and interior of the fibres by removal of a granular calcium compound from the fibres to a specific extent, and (b) the calcium present in the fibres. This invention is, of course, also applicable to conjugated fibres having sheath-core or side-by-side structures.

Moreover, this invention is applicable not only to PVA fibres having a circular cross section but also to those having a cross section of any other shape, such as hitherto been proposed in connection with fibres for reinforcing cement.

The invention will now be described in further detail with reference to Examples, which are illustrative. In the Examples parts and percentages are by weight unless otherwise stated.

Example 1

A 12.92% aqueous solution of polyvinyl alcohol having a polymerisation degree of 1,680 and a saponification degree of 99.9 mol% w as mixed with a 2.52% aqueous dispersion of calcium carbonate, in amount 20% based on PVA, and the mixture was defoamed. A spinning solution having a total solids content of 15.5% was obtained. Calcium carbonate (Whiton P30 of Toyo Fine Chemical Co., Ltd.) was crushed in a wet condition by an attritor of Mitsui-Miike Manufacturing Co., Ltd. into particles having an average particle diameter of 1.8 microns. The spinning solution was spun into a saturated solution of sodium sulphate through a nozzle having a bore diameter of 0.09 mm and solidified, and the resulting fibres were drawn into a wet condition at a draw ratio of 3:1, dried, hot drawn under heat in a dry condition, making a total draw ratio of 7.4:1, and then heat treated, whereby PVA fibres having a denier of 3.4 were obtained.

The fibres were then immersed in a mixed solution containing 130 g of sodium sulphate and 280 g of sulphuric acid per litre at 70°C for half an hour under tension. When the fibres were immersed in the solution, formation of carbon dioxide was observed, indicating the reaction of calcium carbonate. The fibres were then passed through a solution containing 2 g of sodium hydroxide per litre for neutralisation, whereby sulphuric acid and sodium sulphate were removed from the fibres. Thereafter they were washed with water, dried and wound on a support. The fibres thus obtained had a surface as shown in Figure 1, i.e. the fibres had a surface roughened to provide a multiplicity of crack-like concavities, which had never been obtained on any known PVA fibre.

The physical properties of the fibres are shown in Table 1 below.

Table 1

Amount of CaCO_3 prior to sulphuric acid treatment	19.7% of PVA	
Amount of CaCO_3 in terms of Ca after sulphuric acid treatment	14.0% of PVA	
Amount of remaining CaCO_3	71.1% of PVA	60
Void volume after sulphuric acid treatment	0.23 cm^3/g	
Fineness	2.7 denier	

Table 1 (cont.).

Strength	4.3 g/dr	
Elongation	11.9%	
Young's modulus (dry)	105 g/dr	
5 Young's modulus (wet)	10 g/dr	5

The calcium contents of the fibres were determined by titration of a solution of the fibres with ethylenediaminetetra-acetic acid, while Totite BT (Eriochrome Black T) was used as an indicator. Their void volume was determined by a mercury injection method employing a porosimeter.

Examples 2 to 9, and

- 10 **Comparative Examples 1 to 6** 10
A 13.8% aqueous solution of PVA having a polymerisation degree of 1,710 and a saponification degree of 99.9 mole% was mixed with a 3.4% aqueous dispersion of calcium carbonate that was 25% by weight based on PVA, and the mixture was defoamed. A spinning solution having a total solid content of 17.2% was obtained.
- 15 Two kinds of calcium carbonate were used, i.e., heavy calcium carbonate known as Whiton P30 of Toyo Fine Chemical Co. Ltd. and emulsion-type synthetic calcium carbonate known as Brilliant S-15 of Shiraishi Kogyo Co. Ltd. Natural calcium carbonate was crushed in a wet condition for different lengths of time to provide particles having different average particle diameters. 15
- 20 The spinning solution was spun into a saturated solution of sodium sulphate through a nozzle having a bore diameter of 0.09 mm, and solidified. The resulting fibres were drawn in a wet condition at a draw ratio of 3:1, and, after they had been dried, they were drawn under heat in a dry condition at a draw ratio of 2.67:1, making a total draw ratio of 8.0:1. Drawing was followed by heat treatment. 20
- For comparison purposes, spinning solutions containing no calcium carbonate were prepared, and fibre were formed from them under the same conditions as above been set forth.
- 25 Table 2 shows the particle diameters of calcium carbonate used, and the results of evaluation on the operating efficiency. As can be seen from Examples 2 to 5, a satisfactory degree of operating efficiency was obtained in accordance with this invention without any problem in spinnability or drawability if the calcium carbonate had an average particle diameter not exceeding 10 microns. On the other hand, no operating efficiency could be obtained, and no fibre could be made, if calcium 25
- 30 carbonate having an average particle diameter exceeding 10 microns was used. Since it blocked the nozzle during the spinning operation and caused napping and breakage during the drawing operation, as can be seen from Comparative Examples 1 and 2. 30

Table 2

Table 2					
35	Example	Calcium Carbonate Used	Average Particle Dia. of Calcium Carbonate (μ)	Operating Efficiency (Spinnability and Drawability)	35
	2	Whiton P30	0.5	Very satisfactory	
	3	Whiton P30	1.2	Very satisfactory	
	4	Brilliant S-15	2.3	Very satisfactory	
40	5	Whiton P-30	5.6	Satisfactory	40
	Comparative				
	1	Whiton P30	11	Nozzle blocking, and napping	
45	2	Whiton P30	50	Nozzle and filter blocking, and no drawing possible	45
	3	—	—	Very satisfactory	

- 50 The fibres obtained in Example 4 were immersed under tension in a mixed solution containing 280 g of sulphuric acid and 130 g of sodium sulphate per liter at 70°C for different lengths of time, i.e., 1, 5, 10, 30, 60 and 120 minutes, respectively. The solution was circulated to provide a bath ratio of 1:500, whereby calcium carbonate was partially removed by dissolution from the fibres. The results thereby obtained are referred to in Comparative Example 4, and Examples 6 to 10, respectively, in Table 3. The fibres of Comparative Example 3, in which no additive had been incorporated, were also treated in the same way, and the results are shown at Comparative Example 5. Then the fibres were passed through a solution containing 2 g of sodium hydroxide per liter for neutralisation, whereby 55
- 55 sulphuric acid and sodium sulphate were removed from the fibres. After they had been washed with water, the fibres were dried by a hot air drier at 110°C to 170°C for 10 to 20 minutes, and wound on a support. The physical properties of the fibres thus obtained are shown in Table 3.

Table 3

Table 3

5		<i>Acid treating time (min.)</i>	<i>Amount of CaCO₃ prior to acid treatment (% of PVA)</i>	<i>Amount of CaCO₃ after acid treatment in terms of Ca (% of PVA)</i>	<i>Amount of remaining CaCO₃ (% of PVA)</i>	5	
	<i>Example</i>						
	Comparative 4	1	25.1	24.0	95.6		
	Example						
10	6	5	25.2	17.1	67.8	10	
	7	10	25.1	10.5	42.0		
	8	30	24.8	9.2	37.0		
	9	60	24.9	4.1	16.3		
	10	120	25.2	1.5	5.8		
15	Comparative					15	
	5	30	—	—	—		
		<i>Void volume after treatment (cm³/g)</i>	<i>Fineness (denier)</i>	<i>Strength (g/dr)</i>	<i>Elongation (%)</i>	<i>Dry Young's modulus (g/dr)</i>	
20	Comparative 4	0.09	2.7	6.3	8.9	152	20
	Example						
	6	0.15	2.6	6.8	8.8	147	
	7	0.25	2.5	6.4	8.7	150	
	8	0.32	2.3	6.2	8.8	156	
25	9	0.40	2.4	6.0	8.6	150	25
	10	0.49	2.6	5.6	8.7	148	
	Comparative						
	5	0.095	3.0	7.3	8.8	158	

Comparative Example 4 shows the fibres having too small a void volume as a result of too short a time of acid treatment, though they satisfy the requirements of this invention as far as the calcium content of the acid treated fibres is concerned. Comparative Example 5 shows ordinary PVA fibres having too small a void volume despite their acid treatment. All of Examples 6 to 10, in which the time for acid treatment was appropriately selected so as to permit 5 to 95% of calcium to remain in the fibres, satisfy the requirements of this invention both in the calcium content of the fibres and in their void volume. Examination of the fibre surfaces through an electron microscope indicates that the surfaces of the fibres according to Examples 6 to 10 are formed with a multiplicity of differently sized crack-like concavities, including those having a width of 300 mμ to 1 μ and a length which is 5 to 11 times greater than their width, and which extends along the axes of the fibres, those having a smaller width of, say, 30 to 40 mμ, and those having a larger width of, say, 4 μ. These roughened surfaces have never been found on any ordinary PVA fibre.

Figure 2 is an electron microphotograph showing the fibres according to Example 8. The surfaces of the fibres according to Comparative Example 4 are formed with only a very small number of very small cracks, and do not substantially differ from those of any ordinary PVA fibres.

The adhesion to cement of the fibres according to Comparative Examples 4 and 5, and Examples 6 to 8 and 10 of this invention was examined in accordance with the following procedures. The fibres were buried in Portland cement with a water to cement ratio of 0.5, and after the cement was allowed to harden in the air at 25°C for 24 hours, attempts were made to withdraw the fibres, and the length of the fibre portion withdrawn from the cement was measured. The results are shown in Table 4. Then, the fibres were cut to a length of 6 mm, and a cement sheet was prepared from a mixture of fibres, unbleached pulp, chrysotile asbestos 5R and Portland cement having a ratio by weight of 2:5:91. After the cement sheets thus obtained had been cured in the air at 25°C for 14 days, their bending strength was measured, and the adhesion of cement to the fibres was examined by an electron microscope. The results are shown in Table 4.

Table 4

	Example	Fibre length withdrawn from cement (mm)	Bending strength (kg/cm ²)	Adhesion of cement to fibres in cement sheet	
5	Comparative 4	0.92	328	Cement adhering to fibres was very easy to peel off	5
	Example 6	0.38	360	Satisfactory adhesion of cement crystals was observed	
10	7	0.29	365	"	10
	8	0.14	355	"	
	10	0.26	345	"	
	Comparative 5	2.30	302	No adhesion of cement.	

- 15 Table 4 indicates a smaller fibre length withdrawn from cement in the examples of this invention than in the Comparative Examples, and a greater degree of adhesion of cement to the fibres in the cement sheets according to the Examples of this invention. It is, thus, noted that the products according to the Examples of this invention have an improved adhesion between the PVA fibres and the cement, and a greatly improved bending strength, as shown in Table 4, despite the low strength and
- 20 Young's modulus of the fibres *per se*. Figure 3 shows the adhesion of cement to the fibres of Example 7 in a broken surface formed during the aforesaid tests. The growth of cement crystals on the fibres is clearly observed. 20

Example 11

- The fibres of Example 7, from which a certain amount of calcium had been removed by
- 25 dissolution, were immersed under tension in a mixed solution containing 30 g of formalin, 130 g of sulphuric acid and 270 g of sodium sulphate per liter at 70°C and a bath ratio of 1:200 for 10 minutes. Then, the fibres were treated with sodium hydroxide for neutralisation of sulphuric acid, washed with water, and dried, whereby fibres having a formalisation degree of 32% were obtained. The physical properties of the fibres thus obtained are shown in Table 5 below. 25

Table 5

30	Amount of CaCO ₃ in terms of Ca after formalisation	8.3% of PVA	30
	Amount of remaining CaCO ₃	32.0% of PVA	
	Void volume after formalisation	0.33 cm ³ /g	
	Fineness	2.4 denier	
35	Strength	6.0 g/dr	35
	Elongation	8.6%	
	Young's modulus (dry)	152 g/dr	

The fibres were, then, tested for adhesion to cement under the same conditions as hereinabove set forth in Example 6 to 10, and the results as shown in Table 6 were obtained.

Table 6

40	Fibre length withdrawn from cement	0.24 mm	40
	Bending strength	362.0 kg/cm ²	
	Adhesion of cement to fibres in cement sheet	Satisfactory.	
45		Growth of cement crystals observed.	45

The cement slate obtained herein was, then, dipped in water for three days, and its wet bending strength was determined. It showed a bending strength of 384 kg/cm². These results indicate that the formalisation of the reinforcing fibres contributes to maintaining a high water resistance thereof even when they have been wetted, thereby improving their reinforcing efficiency.

50 **Example 12** 50

and Comparative Example 6

- A 20% aqueous dispersion was prepared from desulphurisation gypsum composed of calcium sulphate (dihydrate) containing impurities. The gypsum was formed by wet crushing into particles having an average diameter of 5.4 microns. Completely saponified PVA having a polymerisation degree of 1,690 and a saponification degree of 99.9 ml % was dissolved in water to form 16.0% aqueous solution of PVA defining a spinning solution. The aforesaid gypsum was, then, added into the spinning solution in the quantity of 20% based on pva and mixed therewith, followed by defoaming,
- 55 55

whereby a spinning solution having a total solid content of 16.6% (i.e., a PVA content of 13.8% and a gypsum content of 2.8%) was obtained.

The spinning solution thus obtained was spun into a saturated bath of sodium sulphate through a nozzle having a bore diameter of 0.08 mm, and hardened. The resulting product was drawn at a draw ratio of 4 in a wet condition, and after it had been dried, it was drawn again under heat in a dry condition at a total draw ratio of 7.5, and heat treated.

For comparison purposes, a similar spinning solution but not containing any gypsum, was spun into fibres under the same conditions (Comparison Example 6).

The fibres thus obtained were immersed in a mixed solution containing 50 g of sodium sulphate and 50 g of sodium hydroxide per liter at 70°C for half an hour for removal of calcium by dissolution. Then, the fibres were immersed in a bath containing 2 g of sulphuric acid per liter for neutralisation on sodium hydroxide, washed with carefullly, and dried on rollers at 130°C for 10 minutes.

The physical properties of the fibres thus obtained are shown in Table 7.

Table 7

	<i>Example 12</i>	<i>Comparative Example 6</i>
Amount of CaSO ₄ prior to alkali treatment (% of PVA)	20.2	—
Amount of CaSO ₄ after alkali treatment (% of PVA)	6.9	—
Amount of remaining CaSO ₄ (%)	34.0	—
Void volume (cm ³ /g)	0.31	0.095
Fineness (denier)	3.2	3.1
Strength (g/dr)	5.4	6.1
Elongation (%)	10.1	9.8
Dry Young's modulus (g/dr)	142	168

The fibres were, then, tested for adhesion to cement under the same conditions as set forth in Examples 6 to 10. The results of the tests, as well as the results of examination through an electron microscope, are shown in Table 8.

Table 8

	<i>Example 12</i>	<i>Comparative Example 6</i>
Fibre length withdrawn from cement (mm)	0.28	2.35
Bending strength (kg/cm ²)	361	310
Adhesion of cement to fibres in cement sheet	Great adhesion	No adhesion

The examination of the fibre surfaces through an electron microscope showed that the fibres of Example 12 had as rough a surface as those of Example 1, while the fibres of Comparative Example 6 had a surface which was not different from that of any ordinary PVA fibre. Table 8 indicates a by far smaller fibre length withdrawn from cement in Example 12 than in Comparative Example 6, which testifies an improved adhesion of the fibres according to this invention. Table 8 also indicates a greater contribution of the fibres according to this invention to improving the bending strength of a cement product reinforced therewith.

Examples 13 to 15 and Comparative Examples 7 to 9

A number of spinning solutions each containing 4%, 20% or 40% of synthetic calcium carbonate BRILLIANT S-15 and having a total solid content of 18.6% were prepared from PVA having a polymerisation degree of 1,680 and a saponification degree of 99.9 mol % substantially as hereinabove described. Each spinning solution thus obtained was spun into a saturated bath of sodium sulphate to form fibres. The fibres were drawn at a total draw ratio of 8.5, and had a fineness of 2.3 denier. The fibres were subjected to acid treatment in a mixed solution containing 100 g of sulphuric acid and 100 g of sodium sulphate per liter and having a temperature of 70°C, and immersed in a solution containing 50 g of sodium hydroxide per liter for neutralization of sulphuric acid and dried.

The properties of the fibres thus obtained are shown in Table 9.

Table 9

	Amount of calcium carbonate added (% of PVA)	Amount of Ca remaining in fibres (% of PVA)	Amount of calcium carbonate remain in fibres (% of PVA)	Void volume (cm ³ /g)	Bending strength (kg/cm ²)
Comparative Example					
7	4	0.8	50	0.07	303
8	4	0.08	5	0.14	293
Example					
13	20	0.48	6	0.40	364
14	40	3.0	19	0.38	357
15	40	0.8	5	0.43	368
Comparative Example					
9	40	0.16	1	0.52	302

There was definitely a deficiency of calcium carbonate in Comparative Examples 7 and 8.

According to Comparative Example 7, no satisfactory void volume could be obtained despite the removal of as much as 50% of calcium by dissolution, and only a cement sheet having a low bending strength could be produced. A slightly improved void volume could be obtained in Comparative Example 8, since as much as 95% of calcium was removed by dissolution, but the resulting reduction in the amount of calcium in the fibres could produce a cement sheet having a low bending strength. 20

In Comparative Example 9, in which a sufficiently large quantity of calcium carbonate was employed, the excessive removal of calcium by dissolution brought about a deficiency of calcium in the fibres resulting in a cement sheet having a low bending strength, though the fibres had a satisfactory void volume. 25

Examples 13 to 15 indicate the possibility that a cement sheet having a satisfactorily improved bending strength may be produced if the quantity of calcium carbonate to be employed, and the degree of calcium removal from the fibres fall within the ranges specified by the method of this invention to thereby ensure a satisfactory quantity of calcium remaining in the fibres and a satisfactory void volume thereof. 30

Example 16 and Comparative Example 10

An aqueous PVA solution having a total solid content of 19.5% was prepared by adding 18%, based on PVA, of boric acid into completely saponified PVA having a polymerisation degree of 1,710 and a saponification degree of 99.9 mol %. Desulphurisation gypsum having an average particle diameter of 4.8 microns was dissolved in water to form an aqueous gypsum solution having a solid content of 20%. A spinning solution having a solid content of 19.9% was prepared by adding 40%, based on PVA, of the gypsum solution into the PVA solution, and stirring them together. 35

The spinning solution thus obtained was spun into a mixed aqueous solution containing 50 g of sodium hydroxide and 350 g of sodium sulphate per liter through a nozzle having a bore diameter of 0.1 mm. The fibres thus obtained were treated with sulphuric acid for complete neutralisation of the alkali, washed with water, and drawn at a draw ratio of 5 in a wet condition. After they were dried, the fibres were further drawn under heat until a total draw ratio of 13.5 was reached, and heat treated. 40

For comparison purposes, a PVA spinning solution not containing any gypsum was prepared, and spun into fibres under the same conditions. 45

The fibres thus obtained were immersed under tension in a mixed solution containing 250 g of sulphuric acid and 150 g of sodium sulphate per liter and having a temperature of 70°C for half an hour for removal of calcium by dissolution. After sulphuric acid had been neutralised, the fibres were washed with water and dried. 50

The physical properties of the fibres thus obtained are shown in Table 10.

Table 10

		Example 16	Comparative Example 10	
55	Amount of CaSO ₄ after treatment with sulphuric acid (% of PVA)	9.3	—	55
	Void volume after treatment with sulphuric acid (cm ³ /g)	0.38	0.05	
60	Fineness (denier)	2.3	2.0	60
	Strength (g/dr)	7.6	8.2	
	Elongation (%)	5.0	5.4	
	Young's modulus (g/dr)	229	233	

The fibres were, then, tested for adhesion to cement under the same conditions as set forth in Examples 6 to 10, and the results as shown in Table 11 were obtained.

Table 11

		<i>Example 16</i>	<i>Comparative Example 10</i>	
5	Fibre length withdrawn from cement (mm)	0.33	1.25	5
	Bending strength (kg/cm ²)	365	308	
10	Adhesion of cement to fibres in cement sheet	Great adhesion	Little adhesion	10

Claims

1. Polyvinyl alcohol synthetic fibres obtained by the mixed spinning of polyvinyl alcohol and a granular calcium compound that is insoluble or only sparingly soluble in water, the said fibres having improved adhesion to cement, compared with known polyvinyl alcohol synthetic fibres, and having formed on their surfaces a multiplicity of crack-like concavities formed by elution of the calcium compound after formation of the fibres and extending along the axes of the fibres, the fibres having a void volume of 0.1 to 0.5 cm³/g and containing at least 0.2% by weight of calcium based on polyvinyl alcohol. 15
2. A method of manufacturing polyvinyl alcohol synthetic fibres having improved adhesion to cement, that comprises incorporating a granular calcium compound having particle size of 0.05 to 10 microns and of zero or only sparingly solubility in water into an aqueous solution of polyvinyl alcohol to prepare a mixed spinning solution containing 5 to 50% by weight of the calcium compound based on polyvinyl alcohol, spinning the resulting solution to form fibres, and drawing and heat treating the fibres and immersing them in an acid or alkali to elute the calcium compound so that the fibres may contain at least 0.2% by weight of calcium based on polyvinyl alcohol. 20
3. A method as claimed in Claim 2, in which the calcium compound has a particle size in the range 0.3 to 3 microns. 25
4. A method as claimed in Claim 2 or 3, in which the spinning solution contains 10 to 30% by weight of said calcium compound based on polyvinyl alcohol.
5. A method as claimed in Claim 2, 3 or 4, in which the calcium compound is a substance represented by a chemical formula containing a sulphate, carbonate or silicate group. 30
6. A method as claimed in any one of Claims 2 to 5, in which the drawing is performed to obtain a total draw ratio of 6 to 16.
7. A method as claimed in any one of Claims 2 to 6, in which the fibres are wet-spun using a coagulating bath comprising a highly concentrated aqueous solution of sodium sulphate. 35
8. A method as claimed in any one of Claims 2 to 7, in which the elution is performed to permit the fibres to contain 5 to 95% by weight of calcium based on polyvinyl alcohol.
9. A method as claimed in Claim 2, substantially as hereinbefore described in any one of the foregoing Examples.
10. Cement reinforced by fibres as claimed in Claim 1 or prepared by a method as claimed in any one of Claims 2 to 9. 40